UNITED STATES PATENT AND TRADEMARK OFFICE

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2. That I am well acquainted with the German and English languages.

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4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group plc

The 20th day of April 2004

Description

# Process for etching a substrate

The invention relates to a process in accordance with the preamble of Claim 1.

In the context of the fabrication of semiconductor components, e.g. DRAM memory chips, the object is set of introducing very fine structures into a substrate, such as for example a silicon wafer. Inter alia, etching techniques are used for this purpose, in which layers of the substrate are removed over the entire surface or masked patterns produced by lithography are transferred into the layer below.

One technique which is frequently used in this context is wet-etching, in which the material removed from the substrate is converted into a soluble compound. Dilute hydrofluoric acid (HF) is often used as etchant for silicon wafers. The wet etching is carried out either by means of spray etching or by means of dip etching, with the substrates passing through complex sequences of etching, rinsing and drying steps.

In the context of the fabrication of DRAM memory chips, it is known to subject silicon wafers to a series of process steps in a tank in order to produce structures with high aspect ratios (ratio of the depth or height of the structure to the width of the structure). For example, in the case of what are known as deep trenches for DRAMs, aspect ratios of 50 and above are possible. Wet-chemical process sequences which have an effect on such aspect ratios are, in a known way, in what is known as a point-of-use tank, in which silicon wafers are successively subjected to a first etching step using dilute hydrofluoric acid, a first rinsing step, a second etching step using $NH_4OH$ and a second rinsing step. The silicon wafers are then dried.

The first etching step is used to remove a native oxide layer from the surface of the silicon wafer. The second etching step serves to increase the feature size (widening, fabrication of a bottle structure).

However, if it is desired to transfer these process steps to a bench tool, in which the process steps are carried out sequentially in different tanks, a problem arises on account of the need to transport the silicon wafers between the tanks. After the first etching step using the dilute hydrofluoric acid, the surface of the silicon wafer is hydrophobic, and consequently after the first rinsing step the $NH_4OH$ solution does not make sufficient contact with the silicon surface, and consequently the result of the second etching step is inadequate.

The present invention is based on the object of providing a process which avoids these problems.

According to the invention, this object is achieved by a process having the features of Claim 1.

This involves passing through the following steps:

a) at least one substrate, for a first etching step, is arranged for a predetermined time in a first vessel containing a first etchant, then

b) at least one substrate, for a first rinsing step, is arranged for a predetermined time in a second vessel containing a first rinsing agent, the first rinsing agent containing at least one wetting agent, and then

c) at least one substrate, for a second etching step is arranged for a predetermined time in a third vessel containing a second etchant.

The use of the wetting agent in the first rinsing step allows the subsequent second etch to be carried out more successfully.

It is then advantageous if at least one substrate, after the second etching step, is subjected to a second rinsing step using a second rinsing agent in a fourth vessel. At least one substrate is advantageously subjected to a drying step after the second rinsing step.

It is advantageous for the first etchant to include a hydrofluoric acid fraction. It is also advantageous if the second etchant includes an ammonia hydroxide ($NH_4OH$) fraction. In one particularly advantageous embodiment, the first rinsing agent contains the wetting agent in a concentration in the range from 0.01 to 0.1% by weight.

It is advantageous for at least one structure with an aspect ratio in the range from 10 to 80 to be offered up in the second etching step in order for the feature size to be enlarged. In this context, it is particularly advantageous if the structure is a deep trench structure for a DRAM memory cell. The surface treatment of structures with a large aspect ratio is particularly important, since the long, narrow spacers are difficult for the etchant to reach under certain circumstances.

The invention is explained in more detail below with reference to the figures of the drawings and on the basis of a plurality of exemplary embodiments. In the drawings:

Fig. 1A, B illustrates sectional views through a substrate which has been treated using a known process sequence in a point-of-use

tank (Fig. 1A) and in a bench tool (Fig. 1B);

Fig. 2 shows a flow diagram of an embodiment of the process according to the invention;

Figs 3A,B,C,D diagrammatically depict the effect of one embodiment of the process according to the invention.

Figs 1A, 1B illustrate the result of the identical sequence of process steps in the etching of a silicon wafer as substrate 10, on the one hand in a point-of-use tank process (Fig. 1A), and on the other hand for a bench tool process (Fig. 1B). In neither case is a wetting agent added.

The process steps are in this case: first etching step using dilute hydrofluoric acid, first rinsing step, second etching step using $NH_4OH$, second rinsing step and drying step. The sectional views illustrate the etching result after the drying step.

Fig. 1A reveals highly regular structures 11 (in this case bottle trenches) with a depth of 6.09 µm. The aspect ratio is in this case 44. The same sequence of process steps under identical conditions but using a bench tool results in an unusable result, as can be seen from Fig. 1B. The structures 11 produced in the second etching step are irregular. The reason for this is that after the first etching step using hydrofluoric acid, the surface of the silicon wafer 10 is hydrophobic, and consequently in the second etching step the $NH_4OH$ cannot penetrate through the surface correctly into the deep structures, which leads to the poor etching quality.

This problem is solved by an embodiment of the process according to the invention which is illustrated in

Fig. 2. The first process step is an etching step 1 using dilute hydrofluoric acid to remove the oxide layer on a silicon wafer 10.

The second process step is a first rinsing step 2, in which a wetting agent (surfactant; e.g. the wetting agent Easywet) is added to the first rinsing agent, with the effect that in the second etching step 3 which follows the $NH_4OH$ can penetrate more successfully into the deep structures. In this case, therefore, the wetting agent is used not to clean surfaces, but rather as an aid to the etching of structures.

Then, a second rinsing step 4 is carried out, followed by a drying step 5. The silicon wafer 10 which has been etched in this way can then be processed further.

It is important that in this case the wetting agent is not used to clean the surface, but rather forms part of an etching process.

Figs 3A, B, C, D illustrate the effect of one embodiment of the process according to the invention.

After the first etching step 1, the surface of the silicon wafer 10 is hydrophobic (Fig. 3A), so that an aqueous solution cannot penetrate into structures. This is symbolized by the drop on the silicon wafer. The first rinsing step 2, in which according to the invention a wetting agent is added to the first rinsing agent 12, reduces the surface tension of an aqueous solution (Fig. 3B), so that in the second etching step $NH_4OH$ can penetrate into the structures 11 more successfully (Fig. 3C).

Fig. 3D illustrates the true etching result on the basis of a detail of a trench. By comparison with Fig. 1B, it is clear that in this case an anisotropic etch has been achieved.

Although the process is described here in connection with trench structures, it can also be applied to structures which protrude from the surface of the silicon wafer (e.g. ridges).

The execution of the invention is not restricted to the preferred exemplary embodiments described above. Rather, numerous variants which make use of the process according to the invention even in embodiments of fundamentally different configuration are conceivable.

List of reference symbols

| | |
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| 1 | First etching step |
| 2 | First rinsing step with wetting agent |
| 3 | Second etching step |
| 4 | Second rinsing step |
| 5 | Drying step |
| 10 | Substrate |
| 11 | Structure in the substrate |